PATENT ABSTRACTS OF JAPAN

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(71)Applicant : FUJI XEROX CO LTD
(72)Inventor : IMAI AKIRA
SATO KATSUHIRO
ONO YOSHIYUKI

(54) PHOTOSEMICONDUCTOR ELECTRODEPOTOELECTRIC CONVERSION DEVICE AND POTOELECTRIC CONVERSION METHOD

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a photosemiconductor electrode efficiently usable of solar lightand superior in photoelectric conversion efficiencystability and durability by providing a layer having a perylene derivative represented by a specified formula adsorbed thereto on the base material surface of a metal oxide semiconductor.
SOLUTION: This photosemiconductor electrode has a layer having at least a perylene derivative represented by the formula I adsorbed thereto on the base material surface of a metal oxide semiconductor. In the formulaR represents a divalent hydrocarbon group or a heterocyclic group which may be substituted. Examples of the metal oxide semiconductor include titanium oxidethin oxidetungsten oxidezinc oxideindium oxideniobium oxidestrontium titanate and the like. They may be used alone as a single kind or in combination of two or more kinds thereof. Titanium oxide is particularly preferred from the viewpoint of photoelectric conversion characteristicchemical stabilityease of manufacture and the like. The formstructure and size of the base material are not particularly limitedand can be freely selected according to the purpose.

CLAIMS

[Claim(s)]
[Claim 1]An optical semiconductor electrode having the layer to which a perylene derivative expressed with following general formula (I) to a base material surface of a metal oxide semiconductor at least was made to stick.
General formula (I)
[Formula 1]

R expresses the divalent hydrocarbon group or heterocycle group which may be replaced among general formula (I).
[Claim 2]The optical semiconductor electrode according to claim 1 whose perylene derivative expressed with general formula (I) is a compound expressed with either following general formula (II) and (III).
General formula (II)
[Formula 2]

n expresses the integer of 1-20 among general formula (II).
General formula (III)[Formula 3]

X express a hydrogen atoma halogen atom-CH_3-C_2H_5-OH-OCH_3-OCH_3-OC_2H_5-NH_2-COOHor -NO_2 among general formula (III). m and n express an integer of 0-3 respectively.
[Claim 3]The optical semiconductor electrode according to claim 1 or 2 in which a metal oxide semiconductor is chosen from titanium oxidetin oxidetungstic oxidea zinc oxideindium oxideniobium oxideand strontium titanate.
[Claim 4]The optical semiconductor electrode according to claim 1 or 2 whose metal oxide semiconductor is titanium oxide.
[Claim 5]A photoelectric conversion device which has at least a connecting means which connects an electrode of a couple immersed into an electrolytic solutionand an electrode of this couple so that energization is possibleand is characterized by one side of an electrode of this couple being the optical semiconductor electrode according to any one of claims 1 to 4.
[Claim 6]In a photoelectric conversion method of making an electrode of a couple mutually connected so that energization was possible immersed into an electrolytic solutionand producing a photoelectric conversion reaction by irradiating at least one side of an electrode of this

coupleA photoelectric conversion methodwherein an electrode which irradiates with said light is the optical semiconductor electrode according to any one of claims 1 to 4.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the optical semiconductor electrode to which the specific perylene derivative was made to stick on the surface of a metal oxide semiconductorthe photoelectric conversion device using itand the photoelectric conversion method.
[0002]
[Description of the Prior Art]In recent yearsuse of sunlight attracts attention as an energy resource replaced with fossil fuelssuch as petroleum and coal. As a photoelectric conversion device which transforms light energy into electrical energy directlythe dry type solar cell in which p-n junction was formed on inorganic semiconductorssuch as silicon and gallium arsenideis known widelyand it is already put in practical use as a power supply of the object for remote placesor a portable electronic deviceetc. Howeversince the energy and cost which the manufacture takes are very high in the case of said dry type solar cellthere is a problem that it is difficult to use widely.
[0003]The wet solar cell whichon the other handused the photoelectrochemical reaction which occurs by the interface of a semiconductor and an electrolytic solution as another photoelectric conversion device which transforms light energy into electrical energy is known. Metal oxide semiconductors used in said wet solar cellsuch as titanium oxide and tin oxideAs compared with the silicon used in said dry type solar cellgallium arsenideetc. it can manufacture at far low energy and costand titanium oxide is especially expected as a future energy conversion material from excelling in both sides of a photoelectric transfer characteristic and stability. Howeverit cannot be said that they can use only the ultraviolet radiation which is about 4% of sunlightbut their conversion efficiency is high enough since stable optical semiconductorssuch as titanium oxidehave the band gap as large as not less than 3 eV.
[0004]On the surface of this optical semiconductoras sensitizing dye Thenorganic coloring mattersuch as cyanine dye and a xanthene dyeTo make

organometallic complexessuch as a tris(22'-bipyridyl) ruthenium (II) complexadsorband to carry out spectral sensitization is triedit is known that it is a method effective in improvement in conversion efficiency (T. -- OsaM. FujihiraNature. and 264349 (1976).) Brian O'ReganMichael GratzelNature353736 (1991)JP1-220380Aetc.

[0005]Howeverorganic coloring mattersuch as cyanine dye and a xanthene dyeis not enough in respect of stabilityenduranceetc. and on the other handalthough organometallic complexessuch as an organic ruthenium complexare excellent in fieldssuch as conversion efficiency and stabilitythere is a problem of being expensive. Thereforethe actual condition is efficient and that the cheap photoelectric conversion device is not yet provided by high durability.

[0006]

[Problem(s) to be Solved by the Invention]This invention solves many problems in said formerand makes it a technical problem to attain the following purposes. That isan object of this invention is to provide the optical semiconductor electrodephotoelectric conversion deviceand the photoelectric conversion method of it being efficiently availableand excelling in photoelectric conversion efficiencystabilityenduranceetc. and manufacturing sunlight cheaply and easily.

[0007]

[Means for Solving the Problem]

It is an optical semiconductor electrode having the layer to which a perylene derivative expressed with following general formula (I) to a base material surface of <1> metal oxide semiconductor at least was made to stick.

General formula (I)

[0008]

[Formula 4]

[0009]R expresses the divalent hydrocarbon group or heterocycle group which may be replaced among general formula (I).

The perylene derivative expressed with <2> general-formula (I) is an optical semiconductor electrode given in the above <1> which is a compound expressed with either following general formula (II) and (III).

General formula (II)

[0010]

[Formula 5]

[0011]n expresses the integer of 1-20 among general formula (II).
General formula (III)[0012]
[Formula 6]

[0013]X express a hydrogen atoma halogen atom-CH_3-C_2H_5-OH-OCH_3-OCH_3-OC_2H_5-NH_2-COOHor -NO_2 among general formula (III). m and n express the integer of 0-3 respectively.
<3> metal oxide semiconductors are optical semiconductor electrodes given in the above <1> or <2> chosen from titanium oxidethe tin oxidetungstic oxidea zinc oxideindium oxideniobium oxideand strontium titanate.
<4> metal oxide semiconductors are optical semiconductor electrodes given in the above <1> or <2> which is titanium oxide.
It has at least a connecting means which connects the electrode of the couple immersed into <5> electrolytic solutionsand the electrode of this couple so that energization is possibleand one side of the electrode of this couple is a photoelectric conversion device characterized by being an optical semiconductor electrode of a statement from the above <1> at either of <4>.
<6> In a photoelectric conversion method of making an electrode of a couple mutually connected so that energization was possible immersed into an electrolytic solutionand producing a photoelectric conversion reaction by irradiating at least one side of an electrode of this coupleAn electrode which irradiates with said light is the photoelectric conversion method characterized by being an optical semiconductor electrode of a statement from the above <1> at either of <4>.
[0014](Optical semiconductor electrode) An optical semiconductor electrode of this invention has the layer which made a perylene derivative stick to a base material surface of a metal oxide semiconductor at least.
[0015]- Substrate of a metal oxide semiconductor - As said metal oxide semiconductortitanium oxidetin oxidetungstic oxidea zinc oxideindium oxideniobium oxidestrontium titanateetc. are mentionedfor example. These may be used by an one-sort independent and may use two or more sorts together. Especially in this inventionreasons of a photoelectric transfer characteristicchemical stabilitymanufacture easeetc. to titanium oxide is preferred also in these. There is no restriction in particular about shape of a substrate of said metal oxide semiconductorstructureand a sizeand it can choose suitably according to

the purpose. For exampleit may be a substrate which consists only of metal oxide semiconductorsand may be a substrate which forms coating membrane of a metal oxide semiconductor on an electrode with publicly known tabular [by a transparent electrode by ITO glassNesa glassetc. platinumcopperblack leadetc.] or mesh state electrode etc. In the case of the latter substratethis coating membrane may be provided the whole surface on said publicly known electrodeand may be provided in part.

[0016]- As a perylene derivative in perylene derivative-this inventionwhat is expressed with said general formula (I) is mentioned suitably. In this inventiona compound expressed with either said general formula (II) and (III) is preferred in a perylene derivative expressed with said general formula (I)and a compound specifically expressed with following formula (1) - (14) also in it is more preferred.

[0017]

[Formula 7]

[0018]

[Formula 8]

[0019]The perylene derivative shown by said general formula (I)For exampleit is obtained by making a 34910-perylene tetracarboxylic anhydrideand a general formula and the diamine compound (R expresses among a formula the divalent hydrocarbon group or heterocycle group which may be replaced.) expressed with H_2N-R-NH_2 react. Although said at least 2 Eq (2 Eq or more) of diamine compounds are used to a 34910-perylene tetracarboxylic anhydride on the occasion of said reactionIn order to control the byproduction of polymer or oligomerit is preferred touse 10 Eq or more preferably [using an excessive quantity as much as possible] and generally.

[0020]A perylene derivative expressed with said general formula (I) is easily obtained using a cheap raw materialand moreover is excellent in chemical stabilityenduranceetc. and is excellent in holdout in a base material surface of said metal oxide semiconductorand can carry out spectral sensitization of the optical semiconductor electrode stability and efficient over a long period of time.

[0021](Production of an optical semiconductor electrode) A process of providing coating membrane to which a perylene derivative expressed with said general formula (I) was made sticking in a base material surface of

said metal oxide semiconductorIt is easily attained by immersing a substrate of said metal oxide semiconductor into a solution which dissolved with acid a perylene derivative expressed with this general formula (I) in a solvent.

[0022]What can form a salt of a perylene derivative and fusibility which are expressed with said general formula (I)ssuch as organic acidsuch as inorganic acidsuch as chloridesulfuric acidand phosphoric acidacetic acidbenzoic acidtrifluoroacetic acidtoluenesulfonic acidas said acidfor example is mentioned. These may be used by an one-sort independent and may use two or more sorts together. Also in thesewhen combination with the below-mentioned alcoholic solvent is taken into considerationespecially acetic acid is preferred.

[0023]As said solventpolar aprotic solventssuch as ketone solventsuch as alcoholic solventsuch as methanol and isopropyl alcoholacetoneand methyl ethyl ketonedimethyl sulfoxideand N.N-dimethylformamidewaterthese mixed solventsetc. are mentionedfor example. These may be used by an one-sort independent and may use two or more sorts together. Also in theseespecially alcoholic solvent is preferred.

[0024]Although content of a perylene derivative expressed with said general formula (I) in said solution can be suitably chosen according to the purpose processing condition etc.generally it is about 0.01-1 weight section to said solvent 100 weight section. Since content of said acid in said solution changes with sizes of a substrate of said metal oxide semiconductoretc.according to the purposecan choose suitablybut. At least two or more mol equivalents are required to said 1 mol of perylene derivativesandgenerally they are about 0.1-10 weight sections to said solvent 100 weight section.

[0025]It may carry out by heating to temperature below the boiling point of said solvent if needed in order to perform said immersion at a room temperature or to promote adsorption. After performing said immersionan optical semiconductor electrode of a request which washed a substrate of said metal oxide semiconductor using water or alcoholic solvent preferably and for which a layer to which a perylene derivative expressed with said general formula (I) sticks was formed in the surface arbitrary solvents and by drying is obtained. An optical semiconductor electrode of this invention produced by making it above can be used conveniently for the following photoelectric conversion devices and photoelectric conversion methods of this invention.

[0026](Photoelectric conversion device) A photoelectric conversion device of this invention has at least a connecting means which connects an electrode of a couple immersed into an electrolytic solutionand an

electrode of this couple so that energization is possible. Said photoelectric conversion device may be provided with apparatus suitably selected according to the purpose etc. outside an electrode of said coupleand said connecting means.
[0027]-A pair of electrodes - One side in an electrode of said couple is an optical semiconductor electrode of said this inventionand another side is a counterelectrode. As said counterelectrodeif electrochemically stablethere will be no restriction in particularand according to the purposeit can choose from a publicly known thing suitablyfor examplecan choose from transparent electrodessuch as flat electrodessuch as platinumgoldand black leador ITO glassand Nesa glassetc. suitably according to the purpose.
[0028]- Connecting means - As long as it has a function in which an electrode of said couple can be connected as said connecting means so that energization is possiblethere is no restriction in particular and can choose suitably according to the purposebut. For examplea wire rod which consists of conductive materialssuch as a publicly known leadvarious metalcarbonand a metallic oxidein itselfa platea printed filmor a vacuum evaporation film is mentioned. This connecting means is connected to an electrode of said couple so that energization is possible. A photoelectric conversion device of the above this invention can be used conveniently for a photoelectric conversion method of the following this inventions.
[0029](A photoelectric conversion method) A photoelectric conversion method of this invention makes an electrolytic solution immerse an electrode of a couple mutually connected so that energization was possibleand produces a photoelectric conversion reaction by irradiating at least one side of an electrode of this couple. Those in an electrode of said couple who irradiate with light are the optical semiconductor electrodes of said this inventionand another side is said counterelectrode. Said connecting means can be used for connecting an electrode of this couple so that energization is possible. For this reasonas an electrode of said couple mutually connected so that energization was possiblea photoelectric conversion device of said this invention can be used.
[0030]- Electrolytic solution - Although there is no restriction in particular and it can choose suitably as said electrolytic solutionFor examplesaltssuch as potassium chloridea lithium chloridepotassium carbonateand tetraethylammonium perchlorateNonaqueous solvent solutionssuch as solutionsuch as acidssuch as alkalisuch as sodium hydroxide and potassium carbonatesulfuric acidand chlorideand these

mixturesor alcoholand propylene carbonateetc. are mentioned. These may be used by an one-sort independent and may use two or more sorts together. In this inventiona redox reagent from which it is the purpose of attaining stabilization of the photoelectric current characteristicand also potassium iodidep-benzoquinoneetc. produce an oxidation-reduction reaction reversibly may be added to said electrolytic solution.

[0031](Photoelectric conversion reaction) In a photoelectric conversion device and a photoelectric conversion method of this inventiona photoelectric conversion reaction can be produced as follows. That isan above-mentioned electrodei.e. said optical semiconductor electrodeand said counterelectrode of a couple are first immersed into said nature solution of an electric field. Nextthis optical semiconductor electrode is irradiated with monochromatic light of a 300-650-nm wavelength bandwhite light which includes one in this wavelength band of zonesor multicolor light. Thenlight energy is transformed into electrical energy in this optical semiconductor electrode. At this timeit is changed into electrical energy very efficiently to light energy of visible light of not only ultraviolet radiation of a wavelength band below 300-400 nm but a 400-650-nm wavelength band.

[0032]Even visible light which cannot be used with metallic-oxide independentsuch as titanium oxideby using said optical semiconductor electrode in this invention can use effectivelyAs a resultsynthetic use of lightssuch as sunlightis attained and light energiessuch as sunlightcan be transformed into electrical energy at high efficiency. And in said optical semiconductor electrode to be usedsince coloring matter of a perylene derivative stuck to the surface firmlyand has combined with it and it is not easily desorbed from this optical semiconductor electrodethe characteristic of this optical semiconductor electrode is stabilized for a long period of timecan be maintainedand can always perform a photoelectric conversion reaction efficiently.

[0033]

[Example]Hereafteralthough the example of this invention is describedthis invention is not limited to these examples at all.

[0034](Example 1)

- 25 ml of production-alt.titanic acid tetraisopropyl of the optical semiconductor electrode was gradually added into the mixed solution of 150 ml of pure waterand the concentrated nitric acid 1.54g (specific gravity: 1.38)agitating violently. Temperature up was carried out to 80 **continuing churning furthermorechurning was continued at the temperature for 8 hoursand the milky stable titanium oxide colloidal

solution was obtained. This colloidal solution was condensed to 40 ml at 30 ** under decompression of 30mmHgand the titanium oxide colloidal solution was prepared. Said titanium oxide colloidal solution was coated with the spin coat method on ITO/glass base material as an electrodeand was calcinated at 500 ** for 1 hour. This operation was repeated 3 times and the titanium oxide enveloping layer about 1.0 micrometer thick was formed on this ITO/glass base material. When the crystal structure of the obtained layer was checked with the X-ray diffraction methodit was checked that it is a mixture of an anatase and a rutile type. ITO/glass base material in which said titanium oxide enveloping layer was formedAfter 100 mg of NN'-bis(6'-amino-1'-hexyl)-34910-perylene diimidotetracarboxylic acid (compound expressed above (5)) and 1 ml of glacial acetic acid are immersed in the solution which dissolved in 50 ml of methanol for 1 hourwater washesSubsequentlynatural seasoning was washed and carried out with methanol.

[0035]Thenthe lead 7 was connected on the ITO film with which titanium oxide membrane is not coveredthe substrate end and the terminal area of the lead 7 were covered with the epoxy resinand the optical semiconductor electrode as shown in drawing 1 was produced. the optical semiconductor electrode 1 shown in drawing 1 -- the glass base material 2 top -- the ITO layer 3 and the titanium oxide layer 4 -- andThe pigment layer 5 by NN'-bis(6'-amino-1'-hexyl)-34910-perylene diimidotetracarboxylic acid (compound expressed above (5)) is laminated in this orderThe end of these lamination sides and the terminal area with the lead 7 were covered with the epoxy resin as the adhesive agent 6and have adhered with it.

[0036]- The optical semiconductor electrode 1 produced as mentioned above as shown in production-drawing 2 of a photoelectric conversion deviceThe platinum electrode selected as the counterelectrode 9 and the saturation Carmelo electrode selected as the reference electrode 10 were immersed in the electrolytic solution 11 in the transparent glass cell 13each electrode was connected to the potentiostat 12using the lead 7 as a connecting meansand the photoelectric conversion device was produced. As said electrolytic solution 110.1M sodium sulfate / 0.02M potassium iodide solution was used. The lead 7 is connected to each electrode and energization has become possible. The lead 7 is accommodated in the glass tube 8. As the reference electrode 10this photoelectric conversion device is equipped with the saturated calomel electrode so that energization is possible. The photoelectric conversion device was produced by the above.

[0037]- holding in the photoelectric conversion device obtained by more

than photoelectric conversion reaction -so that the potential of said optical semiconductor electrode may be set to 0V to said reference electrode -- white light (the xenon lamp of 500W.) It irradiated with illumination 4000lux or 550-nm monochromatic light (1 mW/cm^2) from the back side of said optical semiconductor electrode. The value of the photoelectric current by the photoelectric conversion reaction produced at this time was measured with the potentiostat. The measurement result was shown in Table 1.

[0038](Example 2) In Example 1like Example 1the outside which replaced the compound expressed above (5) with the compound expressed above (12) produced the optical semiconductor electrode and the photoelectric conversion devicerespectivelyproduced the photoelectric conversion reactionand measured photoelectric current. The measurement result was shown in Table 1.

[0039](Comparative example 1) In Example 1not using the compound expressed above (5)like Example 1the outside which did not combine coloring matter on said titanium oxide coating film produced the optical semiconductor electrode and the photoelectric conversion devicerespectivelyproduced the photoelectric conversion reactionand measured photoelectric current. The measurement result was shown in Table 1.

[0040](Comparative example 2) In Example 1like Example 1the outside which replaced with erythrosin B the compound expressed above (5) produced the optical semiconductor electrode and the photoelectric conversion devicerespectivelyproduced the photoelectric conversion reactionand measured photoelectric current. The measurement result was shown in Table 1.

[0041]

[Table 1]

[0042]

[Effect of the Invention]According to this inventionmany problems in said former are solvable. According to this inventionthe optical semiconductor electrodephotoelectric conversion deviceand the photoelectric conversion method of it being efficiently availableand excelling in photoelectric conversion efficiencystabilityenduranceetc. and manufacturing sunlight cheaply and easily can be provided.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]Drawing 1 is a section approximate account figure of the optical semiconductor electrode in Example 1.

[Drawing 2]Drawing 2 is an approximate account figure of the photoelectric conversion device of Example 1.

[Drawing 3]Drawing 3 is data in which the ultraviolet and visible absorption spectrum of the optical semiconductor electrode in Example 1 is shown.

[Description of Notations]

1 Optical semiconductor electrode
2 Glass base material
3 ITO layer
4 Titanium oxide layer
5 Pigment layer
6 Adhesive agent
7 Lead
8 Glass tube
9 Counterelectrode
10 Contrast electrode
11 Electrolytic solution
12 Potentiostat
13 Glass cell